

## Supporting Information

# **Mechanisms of Hydrogen Evolution Reaction in Two-Dimensional Nitride MXenes using In Situ X-Ray Absorption Spectroelectrochemistry**

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## Experimental Methods

### Materials Synthesis

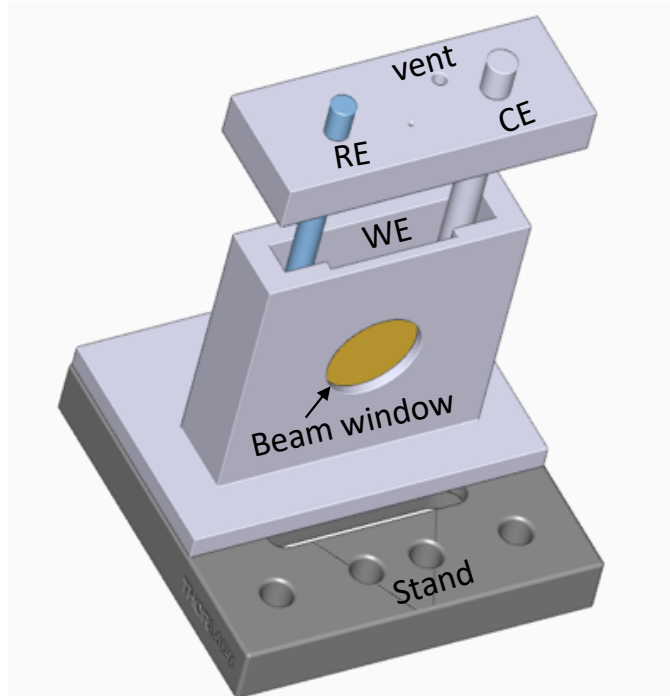
The precursor  $\text{Ti}_4\text{AlN}_3$  MAX phase, exfoliated  $\text{Ti}_4\text{N}_3\text{T}_x$  MXene, and mixed-transition metal nitride  $\text{M-Ti}_4\text{N}_3\text{T}_x$  MXenes were synthesized according to the procedure used in our prior publication.<sup>1</sup>

### In-Situ X-Ray Absorption Spectroscopy

In-situ XAS measurements were performed in a custom-made in-situ electrochemical cell as shown in Figure S1. The working electrodes ( $\text{Ti}_4\text{AlN}_3$  MAX, pristine  $\text{Ti}_4\text{N}_3\text{T}_x$  MXene, and  $\text{M-Ti}_4\text{N}_3\text{T}_x$  MXenes) were prepared by membrane filtration process using an ITO substrate.<sup>1-3</sup> The reference and counter electrodes were Ag/AgCl and graphite rod, respectively. XAS measurements were performed in 0.5 M  $\text{H}_2\text{SO}_4$  electrolytic solution. The electrolyte solution was purged with  $\text{N}_2$  (99.998%) for half an hour prior to adding into the in-situ electrochemical reaction cell. XAS measurements were performed in fluorescence mode at the multi-purpose beamline for spectroscopy, 12-BM at APS. A defined beam size of  $0.5 \times 0.8 \text{ mm}^2$  using slits and an incident photon flux of  $\sim 10^{11} \text{ photons s}^{-1}$  were used. For each material, first, we collected XAS spectra on the dried and wet forms (at the open circuit potential) using a Biologic potentiostat SP300. Prior to the potential-hold XAS measurements, cyclic voltammograms and linear sweep voltammograms were acquired for each sample to ensure that the electrochemical features were consistent with previous work.<sup>1</sup> Next, we collected spectra at four (4) different potentials within the voltage window. After that, we measured XAS at  $-0.5 \text{ V}$  vs. Ag/AgCl, which is in the HER activity region for some but not all of the samples. During each measurement, the nitride MXene material in the in-situ electrochemical cell was held at a constant potential for 15 min prior to the XAS measurements and held at this potential during the XAS data acquisition. Each spectrum

shown in Figure S2a-d is the average of three (3) scans or spectra. Additionally, we collected XAS spectra for bare metal foils as references as shown in Figure S2a-d.

### In-situ X-Ray Absorption Spectroelectrochemical Cell



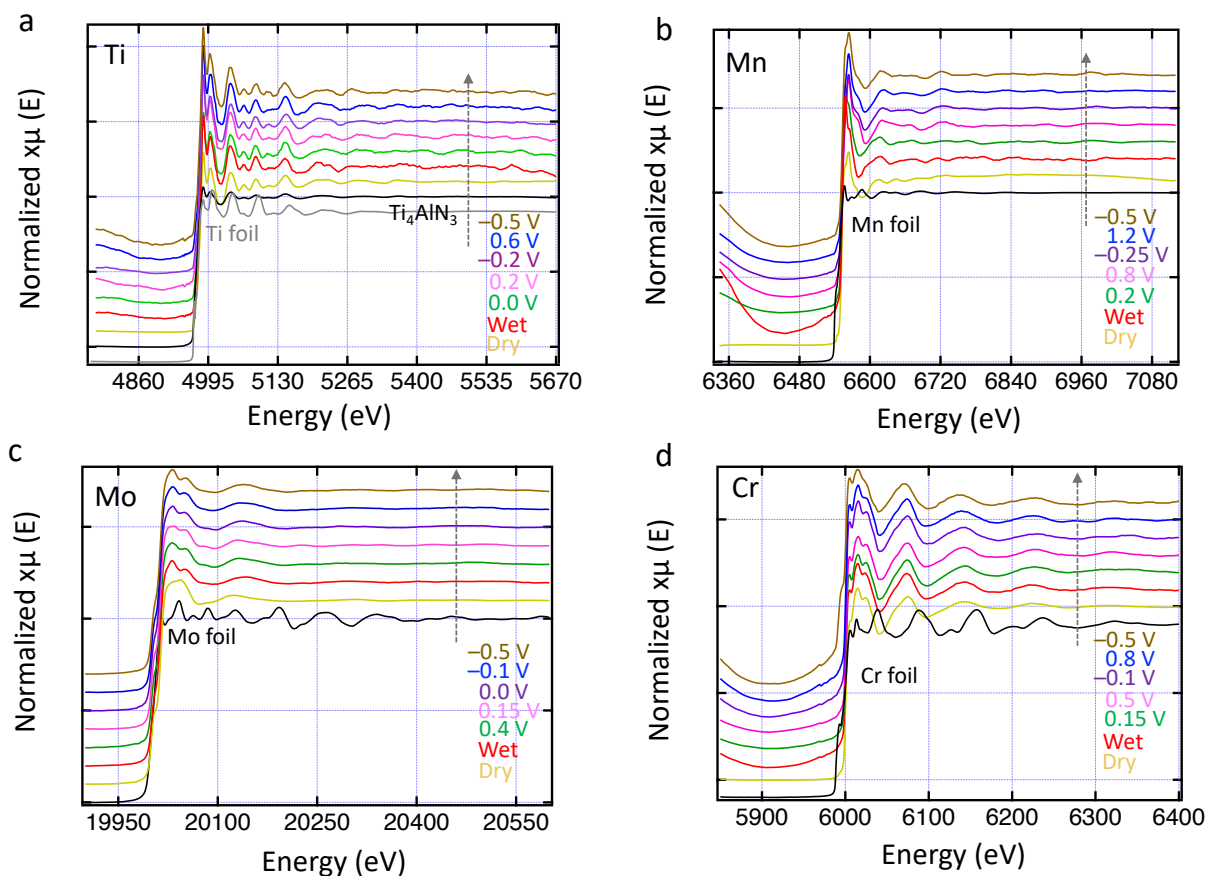
**Figure S1.** In-situ electrochemical cell for the x-ray absorption spectroelectrochemical experiments. RE and CE are the reference electrode (Ag/AgCl, 6 mm) and counter electrode (graphite rod, 7.5 cm long and 6 mm in diameter), respectively. The working electrode (WE) was comprised of exfoliated  $\text{Ti}_4\text{N}_3\text{T}_x$  and M- $\text{Ti}_4\text{N}_3\text{T}_x$  MXenes. Thin coated nitride MXenes on ITO working electrodes ( $\sim 100$  nm thick) were mounted near the window of the in-situ cell. The window was covered with Kapton tape. We observed no scattering from the electrolyte during the XAS measurements.

### **In-situ X-Ray Absorption Spectroelectrochemical Characterization**

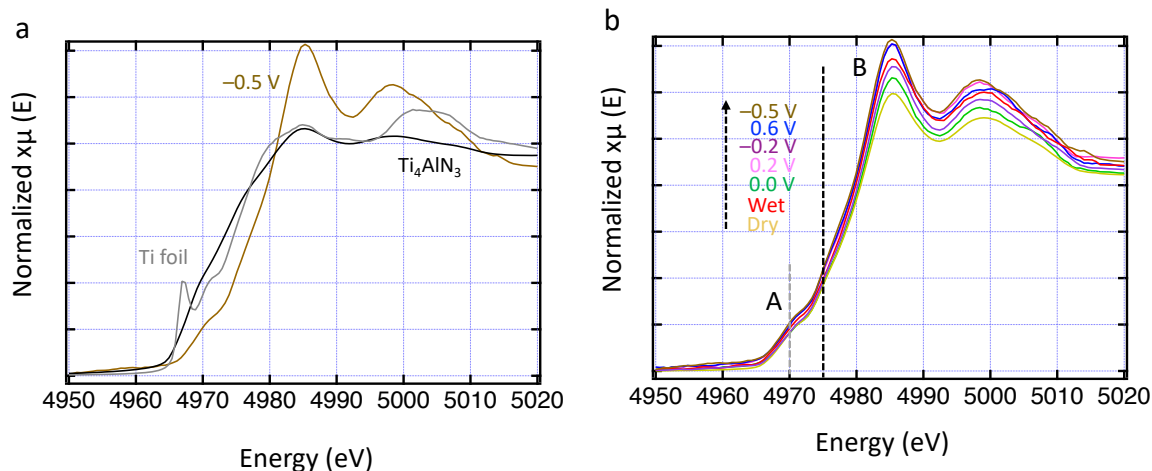
We used in-situ x-ray absorption spectroscopy (XAS) technique to elucidate the mechanisms of hydrogen evolution reaction (HER) activity in two-dimensional (2D) nitride MXenes. Figure S2 shows the normalized fluorescence XAS spectra for the  $\text{Ti}_4\text{AlN}_3$  MAX phase, exfoliated  $\text{Ti}_4\text{N}_3\text{T}_x$  MXene, and mixed-metal  $\text{Mn-Ti}_4\text{N}_3\text{T}_x$ ,  $\text{Mo-Ti}_4\text{N}_3\text{T}_x$ , and  $\text{Cr-Ti}_4\text{N}_3\text{T}_x$  nitride MXenes. Each spectrum shown in Figure S2a-d is the average of three (3) scans or spectra. Additionally, we collect XAS spectra for bare metal foils as references as shown in Figure S2a-d. The spectra in Figure S2a-d show the absorption k-edge energies for Ti, Mn, Mo, and Cr metals and are normalized to the initial absorption energy,  $E_0$ . The k-edge absorption energy  $\mu(E)$  shown here for the Ti, Mn, Mo, and Cr metals are directly proportional to the ratio of the fluorescence intensity leaving the material,  $I_f$ , and the initial intensity going into the material,  $I_0$ , according to the following equation: <sup>4</sup>

$$\mu(E) \propto I_f/I_0 \quad (1)$$

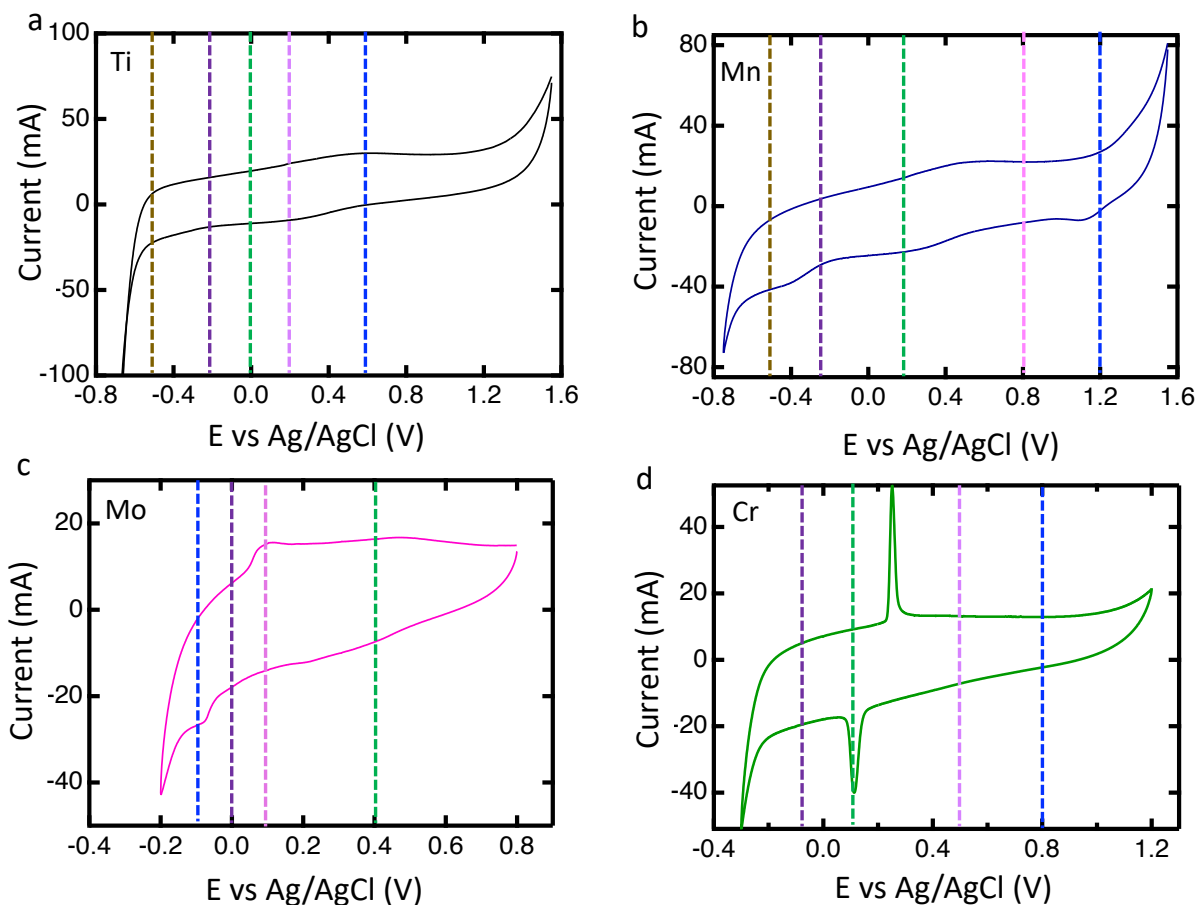
The intensity of the  $I_0$  was measured by using an ion chamber. The XAS spectra in Figure S2a-d are comprised of the x-ray absorption near-edge structure (XANES) and the extended x-ray absorption fine structure (EXAFS) and contain information on the changes in the electronical and structural properties in the nitride MXenes during electrochemical performance and catalytic HER activity. <sup>4</sup>



**Figure S2.** Normalized x-ray absorption spectroscopy (XAS) data for (a) pristine  $\text{Ti}_4\text{N}_3\text{T}_x$ , (b) Mn- $\text{Ti}_4\text{N}_3\text{T}_x$ , (c) Mo- $\text{Ti}_4\text{N}_3\text{T}_x$ , and (d) Cr- $\text{Ti}_4\text{N}_3\text{T}_x$  MXenes, showing the Ti, Mn, Mo, and Cr k edge energy, respectively. First, we collected XAS spectra for dry and wet samples, then, under operating conditions at different potentials in 0.5 M  $\text{H}_2\text{SO}_4$  electrolytic solution. For the spectra collected under operating conditions, the pristine  $\text{Ti}_4\text{N}_3\text{T}_x$  MXene and M- $\text{Ti}_4\text{N}_3\text{T}_x$  MXenes were held at a constant potential for 15 min before the XAS measurement and held at the set potential while we collected the XAS spectra. The XAS spectrum for the precursor  $\text{Ti}_4\text{AlN}_3$  MAX phase is also shown (black spectrum in (a)). Additionally, we collected XAS spectra for bare metal foils as references as shown in (a-d). For all the materials, the spectrum (brown color) for the potential hold experiment at -0.5 V versus Ag/AgCl (V) is used to probe the HER XAS. We used Ag/AgCl and graphite rod as reference and counter electrodes, respectively.

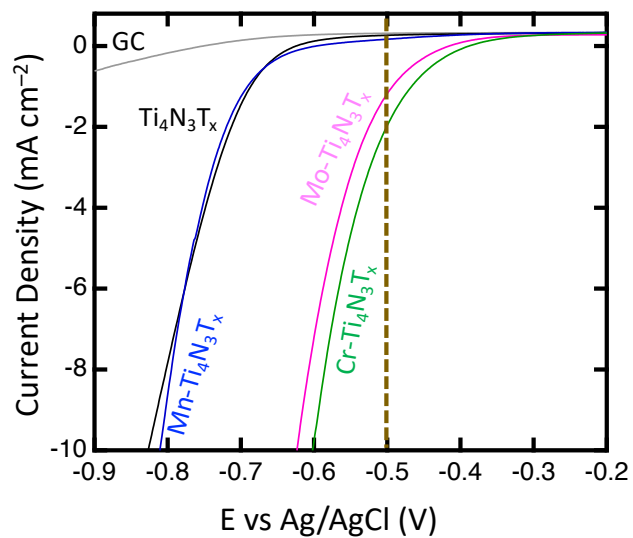


**Figure S3.** Normalized x-ray absorption near edge structure (XANES) for overlaid normalized XANES spectra for (a)  $\text{Ti}_4\text{AlN}_3$  MAX phase (grey), dry (gold spectrum), and  $-0.5$  V vs. RHE (V) (brown), and for (b) different potentials in  $0.5$  M  $\text{H}_2\text{SO}_4$  electrolyte for pristine  $\text{Ti}_4\text{N}_3\text{T}_x$ . The grey and black dashed lines denote the pre-edge and edge energies, respectively. We used Ag/AgCl and graphite rod as reference and counter electrodes, respectively.



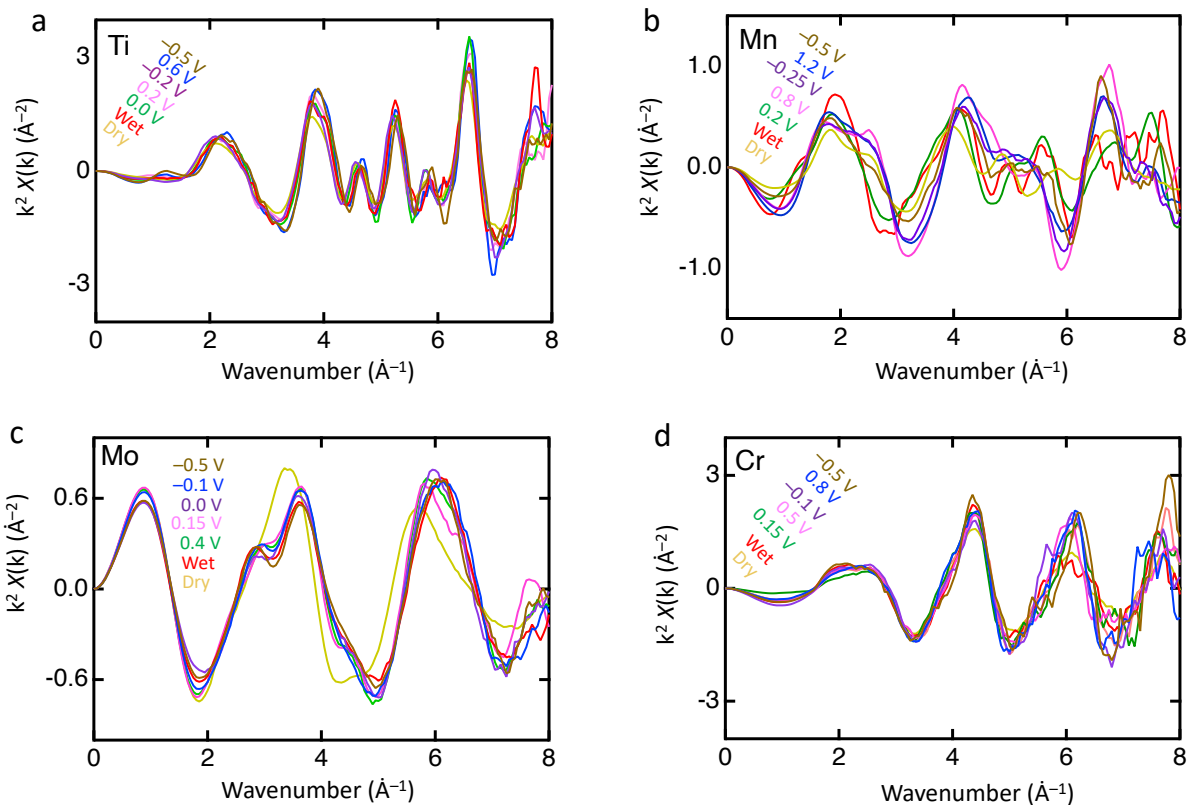
**Figure S4.** Cyclic voltammograms for (a)  $\text{Ti}_4\text{N}_3\text{T}_x$  (black), (b)  $\text{Mn-Ti}_4\text{N}_3\text{T}_x$  (blue), (c)  $\text{Mo-Ti}_4\text{N}_3\text{T}_x$  (pink), and (d)  $\text{Cr-Ti}_4\text{N}_3\text{T}_x$  (green) in 0.5 M  $\text{H}_2\text{SO}_4$  electrolyte at  $50 \text{ mV s}^{-1}$  adapted from reference.

<sup>1</sup> The in-situ XAS measurements were taken at the dashed lines shown in the voltammograms. The brown dashed line at  $-0.5 \text{ V}$  in panels a and b used for the HER XAS measurement is outside of the voltage window for Cr- and Mo- $\text{Ti}_4\text{N}_3\text{T}_x$  MXenes (panels c and d).



**Figure S5.** Linear sweep voltammetry for bare glassy carbon (grey), exfoliated  $\text{Ti}_4\text{N}_3\text{T}_x$  MXene (black),  $\text{Mn-Ti}_4\text{N}_3\text{T}_x$  (blue),  $\text{Mo-Ti}_4\text{N}_3\text{T}_x$  (pink), and  $\text{Cr-Ti}_4\text{N}_3\text{T}_x$  (green) in 0.5 M  $\text{H}_2\text{SO}_4$  electrolyte solution at  $5 \text{ mV s}^{-1}$  adapted from reference.<sup>1</sup> The brown dashed line indicates the potential used for the in-situ XAS measurement taken at the HER region for the  $\text{Mo-Ti}_4\text{N}_3\text{T}_x$  and  $\text{Cr-Ti}_4\text{N}_3\text{T}_x$  samples.





**Figure S6.** K-space spectra for dry (gold spectrum), wet (red spectrum) and different potentials in 0.5 M  $\text{H}_2\text{SO}_4$  electrolyte for (a) pristine  $\text{Ti}_4\text{N}_3\text{T}_x$ , (b)  $\text{Mn-Ti}_4\text{N}_3\text{T}_x$ , (c)  $\text{Mo-Ti}_4\text{N}_3\text{T}_x$ , and (d)  $\text{Cr-Ti}_4\text{N}_3\text{T}_x$  MXenes. We used Ag/AgCl and graphite rod as reference and counter electrodes, respectively. We used a K weight of 2.

### In-situ Extended X-Ray Absorption Fine Structure

The EXAFS spectra for the pristine exfoliated Ti<sub>4</sub>N<sub>3</sub>T<sub>x</sub> nitride MXene were fitted to the EXAFS equation using FEFF and IFEFFIT in Artemis software. <sup>4</sup>

$$\chi(k) = S_0^2 \sum_i N_i \frac{|f_i(k)|}{kR_i^2} e^{(-2\sigma_i^2 k^2)} e^{(-2R_i/\lambda(k))} \sin(2kR_i + 2\delta_i + \varphi_i) \quad (2)$$

Where  $S_0^2$  is the amplitude reduction factor,  $N_i$  is the number of scattering atoms,  $f_i(k)$  is the scattering amplitude,  $R_i$  is the distance from the central atom to the scattering atom, the exponent terms account for the disorder in the position of the atoms and scattered photoelectron vertically over a short distance,  $\delta_i$  is the phase shift undergone by the photoelectron at the central atom, and  $\varphi_i$  is the phase shift undergone by the photoelectron when it bounces off the scattering atom. <sup>4</sup>

**Table S1.** Fitting parameters from the IFEFF simulation from Artemis software for the pristine exfoliated Ti<sub>4</sub>N<sub>3</sub>T<sub>x</sub> MXene at different conditions, R-factor < 0.03.

Electrode	Scattering path & N	Amplitude $S_0^2$	Bond strength ( $\sigma^2$ )	Distance from Ti R (Å)
Dry	Ti–N (3)	0.703	0.00182	2.06922
	Ti–Ti (6)	0.703	0.00191	2.99781
	Ti–N–Ti–N (3)	0.703	0.00514	4.14660
Wet	Ti–N (3)	0.955	0.00397	2.10830
	Ti–Ti (6)	0.955	0.00141	3.03220
	Ti–N (6)	0.955	0.00512	3.77450

Electrode	Scattering path & N	Amplitude $S_o^2$	Bond strength ( $\sigma^2$ )	Distance from Ti R (Å)
0 V	Ti–N (3)	0.832	0.00184	2.05137
	Ti–Ti (6)	0.832	0.00153	2.99025
	Ti–N–Ti–N (3)	0.832	0.00573	4.10119
0.2 V	Ti–N (3)	0.926	0.00004	2.06073
	Ti–Ti (6)	0.926	0.00255	2.99493
	Ti–N–Ti–N (3)	0.926	0.00390	4.10213
–0.2 V	Ti–N (3)	0.752	0.00107	2.05940
	Ti–Ti (6)	0.752	0.00045	2.98465
	Ti–N–Ti–N (3)	0.752	0.00321	4.07087
0.6 V	Ti–N (3)	0.917	0.00123	2.07266
	Ti–Ti (6)	0.917	0.00091	3.00772
	Ti–N–Ti–N (3)	0.917	0.00389	4.10476
–0.5 V	Ti–N (3)	1.074	0.00432	2.07050
	Ti–Ti (6)	1.074	0.00487	2.99852
	Ti–N–Ti–N (3)	1.074	0.00553	4.10117

## References

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